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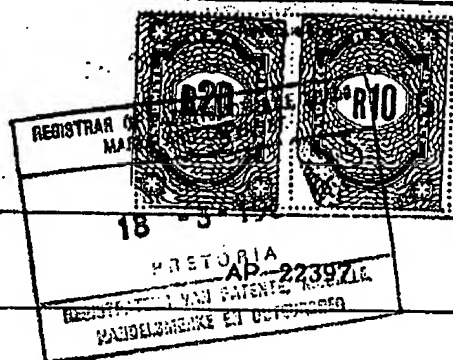
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**John & Kernick**

FORM P 1

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
APPLICATION FOR A PATENT AND  
ACKNOWLEDGEMENT OF RECEIPT  
(Section 30(1) — Regulation 22)

The grant of a patent is hereby requested by the undermentioned applicant on the present application filed in duplicate.

Official application No.  
21 01 831896

J &amp; K Ref:

71 Full name(s) of applicant(s) .....

BAYER AKTIENGESSELLSCHAFT. A legal body organised and existing under the laws of the Federal Republic of Germany.

Address(es) of applicant(s) .....

D-5090 Leverkusen, Germany.

54 Title of invention

OPTICALLY ACTIVE PHENOXYBENZOIC ACID DERIVATIVES, A PROCESS FOR THEIR PREPARATION, AND THEIR USE AS HERBICIDES.

☒  
☐  
☐

The applicant claims priority as set out on the accompanying form P2

This application is for a patent of addition to Patent / Application No.

This application is a fresh application in terms of section 37 and based on Application No.

24	01	
21	01	

This application is accompanied by:

<input type="checkbox"/>	1a
<input checked="" type="checkbox"/>	1b
<input type="checkbox"/>	2a
<input type="checkbox"/>	2b
<input checked="" type="checkbox"/>	3
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<input checked="" type="checkbox"/>	10
<input type="checkbox"/>	11
<input type="checkbox"/>	12
<input type="checkbox"/>	13a
<input type="checkbox"/>	13b

1a A single copy of a provisional specification of ..... pages

1b Two copies of a complete specification of 1.7 pages

2a Informal drawings of ..... sheets

2b Formal drawings of ..... sheets

3. Publication particulars and abstract (form P8 in duplicate)

4. A copy of Figure ..... of the drawings for the abstract

5. Assignment of invention (from the inventors) or other evidence of title

6. Certified priority documents ( / documents)

7. Translation of priority documents ( / documents)

8. Assignment of priority rights

9. A copy of the form P2 and the specification of S.A. Patent Application 21 01

21	01	
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10. A declaration and power of attorney on form P3

11. Request for ante-dating on form P4

12. Request for classification on form P9

13a Request for delay of acceptance on form P4

13b

74 Address for service: JOHN &amp; KERNICK, JOHANNESBURG / PRETORIA.

Date: .....

18 MAR 1983

For the Applicant

The duplicate will be returned to the applicant's address for service as proof of lodging but is not valid unless endorsed with official stamp.

REGISTRAR OF PATENTS, DESIGNS, TRADE MARKS AND COPYRIGHT

Received

18 MAR 1983

PRETORIA

REGISTRAR VAN PATENTE, TEKENINGE, HANDELSMERKE EN OORKEENRECHTE

Registrar of Patents

J. & K. & Co.

FORM P 7

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978

# Complete Specification

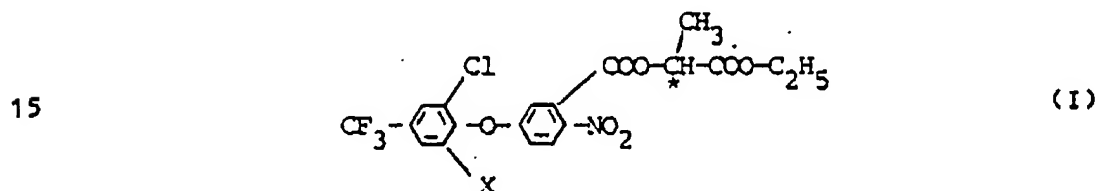
(Section 30(1) — Regulation 28)

21	01	Official application No. <b>831896</b>	22	Lodging date <b>1983-03-10</b>	J&K reference <b>AP 22397</b>
51	International classification  <b>C07C</b>				
71	Full Name(s) of applicant(s)  <b>BAYER AKTIENGESELLSCHAFT.</b>				
72	Full Name(s) of inventor(s)  <b>Reimer Cölln; Ludwig Eue; Robert R. Schmidt.</b>				
54	Title of invention  <b>OPTICALLY ACTIVE PHENOXYBENZOIC ACID DERIVATIVES, A PROCESS FOR THEIR PREPARATION, AND THEIR USE AS HERBICIDES.</b>				

The invention relates to new dextrorotatory enantiomers\*) of phenoxybenzoic acid derivatives, a process for their preparation, and their use as herbicides.

It has already been disclosed that racemates of the compounds 1-ethoxycarbonylethyl 5-(2-chloro-4-trifluoromethyl-phenoxy)-2-nitro-benzoate and 1-ethoxycarbonylethyl 5-(2,6-dichloro-4-trifluoromethyl-phenoxy)-2-nitro-benzoate can be employed for combating weeds (see DE-OS [German Published Specification] 2,950,401 and DE-OS [German Published Specification] 3,029,728). The activity of these substances is good, but the selective herbicidal properties are not always completely satisfactory.

The new dextrorotatory enantiomers of the phenoxybenzoic acid derivatives of the formula

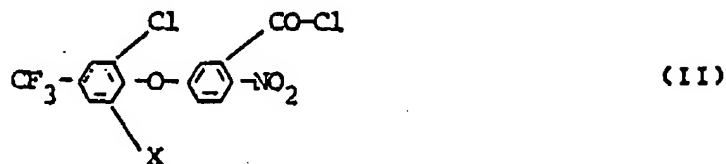


in which

X represents hydrogen or chlorine, have now been found.

Furthermore, it has been found that the new dextrorotatory enantiomers of the phenoxybenzoic acid derivatives of the formula (I) are obtained when phenoxybenzoic acid-chlorides of the formula

\*) Dextrorotatory enantiomers are to be understood here as meaning in each case those optically active compounds which rotate the plane of vibration of linearly polarised light towards the right hand. Said compounds, in this case, show the S-configuration at the asymmetrically substituted carbon atom.



in which

X has the meaning given above,  
are reacted with the laevorotatory enantiomer of ethyl  
5 lactate of the formula



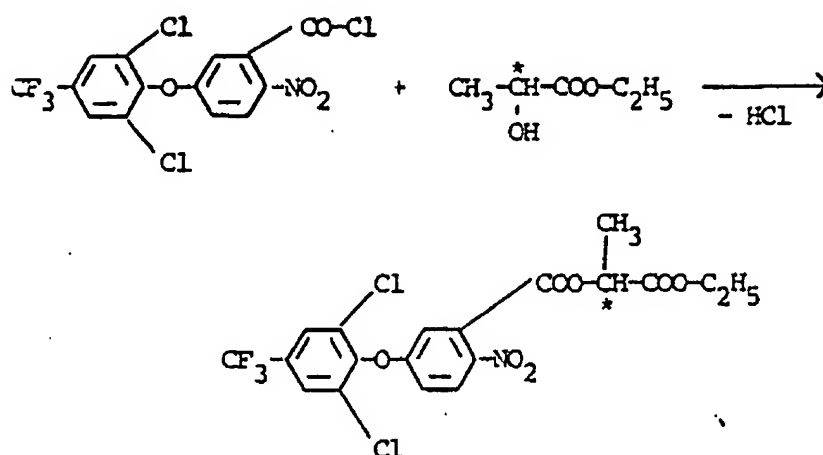
if appropriate in the presence of an acid acceptor and if  
appropriate in the presence of a diluent.

10 Finally, it has been found that the new dextro-  
rotatory enantiomers of the phenoxybenzoic acid derivatives  
of the formula (I) are distinguished by an outstanding herbi-  
cidal activity.

Surprisingly, the new dextrorotatory enantiomers of  
the phenoxybenzoic acid derivatives of the formula (I)  
15 possess substantially better herbicidal properties than the  
corresponding racemic compounds which are known from the  
prior art to be highly active herbicides.

Formula (I) gives a definition of the compounds  
according to the invention. In this formula, the asymmetric  
20 carbon atom is characterised by a (\*).

If 5-(2,6-dichloro-4-trifluoromethyl-phenoxy)-2-  
nitrobenzoic acid-chloride and the laevorotatory enantiomer  
of ethyl lactate are used in the process according to the  
invention, the course of the reaction can be represented by  
25 the following equation:



Formula (II) gives an unambiguous definition of the phenoxybenzoic acid-chlorides required as starting materials in the process according to the invention. In this formula, X represents hydrogen or chlorine.

The phenoxybenzoic acid-chlorides of the formula (II) are known (see DE-OS [German Published Specification] 2,950,401).

The laevorotatory enantiomer of ethyl lactate which is furthermore required as a starting material in the process according to the invention is likewise known: the compound has a specific rotation of  $[\alpha]_{\text{D}}^{20} = -12^\circ$  (neat) and a refractive index of  $n_{\text{D}}^{20} = 1.4130$ .

The process, according to the invention, for the preparation of the new dextrorotatory enantiomers of the phenoxybenzoic acid derivatives of the formula (I) is preferably carried out using diluents. Virtually all inert organic solvents are suitable as such diluents. These include in particular aliphatic and aromatic, optionally halogenated hydrocarbons, such as pentane, hexane, heptane, cyclohexane, petroleum ether, benzine, ligroin, benzene, toluene, xylene, methylene chloride, ethylene chloride, chloroform, carbon tetrachloride, chlorobenzene and

o-dichlorobenzene, ethers, such as diethyl ether and dibutyl ether, glycol dimethyl ether and diglycol dimethyl ether, tetrahydrofuran and dioxane, ketones, such as acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone, esters, such as methyl acetate and ethyl acetate, nitriles, such as, for example, acetonitrile and propionitrile, amides, such as, for example, dimethylformamide, dimethylacetamide and n-methyl-pyrrolidone, as well as dimethyl sulphoxide, tetramethylenesulphone and hexamethylphosphoric acid triamide.

The reaction according to the invention is furthermore preferably carried out in the presence of an acid-binding agent. All customary acid-binding agents can be employed as acid acceptors for this reaction. Preferred compounds are alkali metal hydroxides, such as, for example, sodium hydroxide and potassium hydroxide, alkali metal carbonates and alkali metal alcoholates, such as sodium carbonate and potassium carbonate, sodium methylate, potassium methylate, sodium ethylate and potassium ethylate, and also aliphatic, aromatic or heterocyclic amines, for example triethylamine, trimethylamine, dimethylaniline, dimethylbenzylamine and pyridine.

The reaction temperature can be varied within a relatively wide range. In general the reaction is carried out at between  $-20$  and  $+100^{\circ}\text{C}$ , preferably between  $0$  and  $+50^{\circ}\text{C}$ .

The process according to the invention is carried out in general under atmospheric pressure.

To carry out the process according to the invention, the starting materials are employed in general in approximately equimolar amounts. The reaction is carried out in general in a suitable diluent, in the presence of an acid acceptor, and the reaction mixture is stirred for several hours at the required temperature. The subsequent working-up is effected according to customary methods.

The active compounds according to the invention

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influence plant growth and can therefore be used as defoliants, desiccants, agents for destroying broad-leaved plants and germination inhibitors, and especially as weedkillers. By weeds, in the broadest sense, there are to be understood all plants which grow in locations where they are undesired. Whether the substances according to the invention act as total or selective herbicides depends essentially on the amount used.

10           The active compounds according to the invention can be used, for example, in connection with the following plants:

Dicotyledon weeds of the genera: Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, 15 Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Papaver and Centaurea.

20 Dicotyledon cultures of the genera: Gossypium, Glycine, Beta, Daucus, Phaseolus, Pisum, Solanum, Linum, Ipomoea, Vicia, Nicotiana, Lycopersicon, Arachis, Brassica, Lactuca, Cucumis and Cucurbita.

Monocotyledon weeds of the genera: Echinochloa, Setaria, 25 Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Ischaemum, Sphegoclea, Dactyloctenium, Agrostis, Alopecurus and Apera.

30 Monocotyledon cultures of the genera: Oryza, Zea, Triticum, Hordeum, Avena, Secale, Sorghum, Panicum, Saccharum, Ananas, Asparagus and Allium.

35           However, the use of the active compounds according to the invention is in no way restricted to these genera, but also extends in the same manner to other plants.

La A 21 598



The compounds are suitable, depending on the concentration, for the total combating of weeds, for example on industrial terrain and rail tracks, and on paths and squares with or without tree plantings.

5 Equally, the compounds can be employed for combating weeds in perennial cultures, for example afforestations, decorative tree plantings, orchards, vineyards, citrus groves, nut orchards, banana plantations, coffee plantations, tea plantations, rubber plantations, oil palm  
10 plantations, cocoa plantations, soft fruit plantings and hopfields, and for the selective combating of weeds in annual cultures.

The active compounds can be converted to the customary formulations, such as solutions, emulsions,  
15 wettable powders, suspensions, powders, dusting agents, soluble powders, granules, suspension-emulsion concentrates, natural and synthetic materials impregnated with active compound, and very fine capsules in polymeric substances.

20 These formulations are produced in known manner, for example by mixing the active compounds with extenders, that is, liquid solvents and/or solid carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents, and/or foam-forming agents. In the case of the use of water as  
25 an extender, organic solvents can, for example, also be used as auxiliary solvents. As liquid solvents, there are suitable in the main: aromatics, such as xylene, toluene or alkyl naphthalenes, chlorinated  
30 aromatics or chlorinated aliphatic hydrocarbons, such as chlorobenzene, chloroethylene or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their esters, ketones,  
35 such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strong polar solvents such

as dimethylformamide and dimethylsulphoxide, as well as water.

As solid carriers there are suitable: for example ground natural minerals, such as kaolins, 5 clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates; as solid carriers for granules there are suitable: for example crushed and fractionated natural 10 rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; as emulsifying and/or foam-forming agents 15 there are suitable: for example non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkylsulphates, arylsulphonates as well as albumin hydrolysis products; as dispersing agents there are suitable: 20 for example lignin-sulphite waste liquors and methyl-cellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, 25 granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulations.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and 30 Prussian Blue; and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain between 35 0.1 and 95 per cent by weight of active compound, preferably between 0.5 and 90%.

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7 The active compounds according to the invention,  
as such or in the form of their formulations, can  
also be used, for combating weeds, as mixtures with  
known herbicides, finished formulations or tank mixing  
5 being possible. Mixtures with other known active com-  
pounds, such as fungicides, insecticides, acaricides,  
nematicides, bird repellants, growth factors, plant  
nutrients and agents which improve soil structure,  
are also possible.

10 The active compounds can be used as such,  
in the form of their formulations or in the use forms  
prepared therefrom by further dilution, such as ready-  
to-use solutions, suspensions, emulsions, powders  
and granules. They are used in the customary  
15 manner, for example by watering, spraying, atomising  
or scattering.

The active compounds according to the invention  
can be applied either before or after emergence of  
the plants.

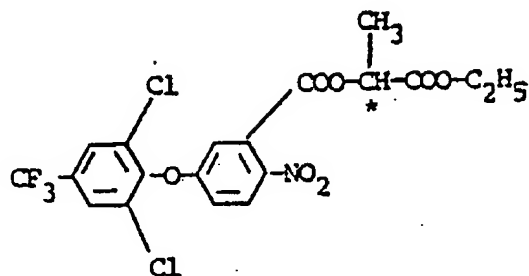
20 They are preferably applied before emergence  
of the plants, that is to say by the pre-emergence  
method. They can also be incorporated into the soil  
before sowing.

The amount of active compound used can vary  
25 within substantial ranges. It depends essentially  
on the nature of the desired effect. In general, the  
amounts used are between 0.05 and 10 kg of active compound  
per ha, preferably between 0.1 and 5 kg/ha.

The preparation and the use of the substances  
30 according to the invention are evident from the examples  
which follow.

Preparation examples

Example 1



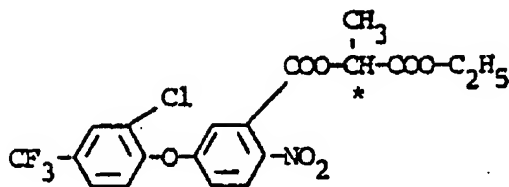
- 446.3 g (3.779 mols) of the laevorotatory enantiomer of ethyl lactate ( $[\alpha]_D^{20} = -12^\circ\text{C}$  (neat);  $n_D^{20} = 1.4130$ ) together with 404 g (4 mols) of triethylamine in 6 litres of toluene are initially introduced. A solution of 1,566 g (3.778 mols) of 5-(2,6-dichloro-4-trifluoromethylphenoxy)-2-nitro-benzoic acid-chloride in 3 litres of toluene is added in the course of 30 minutes at  $0-5^\circ\text{C}$ , while cooling externally and stirring. Thereafter, the mixture is stirred for a further 16 hours at  $20-25^\circ\text{C}$  and then worked up. For this purpose 5 litres of saturated, aqueous sodium chloride solution are added to the reaction mixture, and the phases are separated. The organic phase is washed successively with a mixture of 5 litres of saturated, aqueous sodium chloride solution and 1 litre of hydrochloric acid, then with 5 litres of 5% strength aqueous sodium bicarbonate solution and finally with 5 litres of water. Thereafter, the organic phase is evaporated down under reduced pressure at a bath temperature of  $50^\circ\text{C}$ . The residue which remains is freed from the last volatile constituents by heating for one hour at  $50$  to  $60^\circ\text{C}$  in a high vacuum. In this manner, 1,720 g (98.6% of theory) of the dextrorotatory enantiomer of 1-ethoxycarbonyl-ethyl 5-(2,6-dichloro-4-trifluoro-methyl-phenoxy)-2-nitro-benzoate are obtained.

Melting point:  $53^\circ\text{C}$

Specific rotation:  $[\alpha]_D^{20} = +16.1^\circ$  (1 molar solution in chloroform; cell length = 10 cm).

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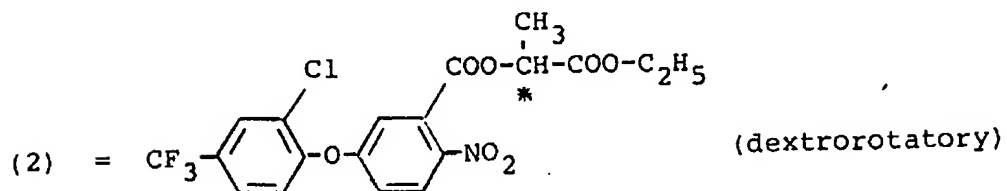
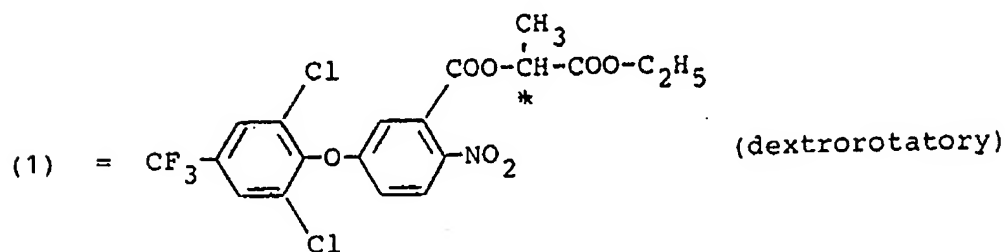
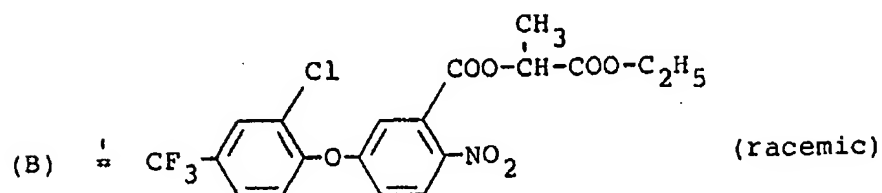
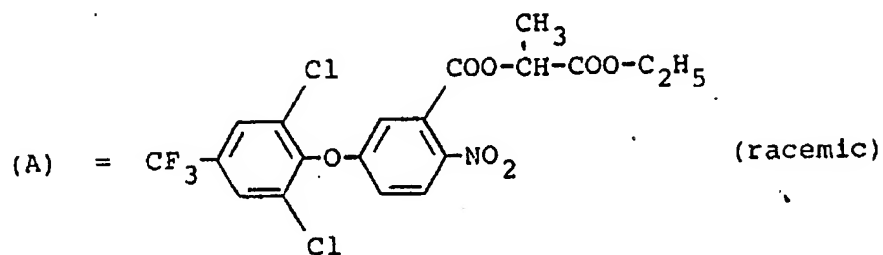
Example 2



828 g (7 mols) of the laevorotatory enantiomer of ethyl lactate ( $[\alpha]_D^{20} = -12^\circ$  (neat);  $n_D^{20} = 1.4130$ ) together with 778 g (7.7 mols) of triethylamine in 11 litres of toluene are initially introduced. A solution of 2,660 g (7 mols) of 5-(2-chloro-4-trifluoromethylphenoxy)-2-nitro-benzoic acid-chloride in 4.5 litres of toluene is added in the course of 35 minutes at 0-5°C, while cooling externally and stirring. Thereafter, the mixture is stirred for a further 16 hours at 20-25°C and then worked up. For this purpose, dilute, aqueous hydrochloric acid is added to the reaction mixture and the phases are separated. The organic phase is washed twice with water and, after it has been dried over sodium sulphate, is evaporated down under reduced pressure. The residue which remains is freed from the last volatile constituents by heating for one hour at 50 to 60°C in a high vacuum. In this manner, 2,740 g (85% of theory) of the dextrorotatory enantiomer of 1-ethoxycarbonyl-ethyl 5-(2-chloro-4-trifluoromethyl-phenoxy)-2-nitro-benzoate are obtained.

Specific rotation:  $[\alpha]_D^{20} = +11.5^\circ$  (1 molar, solution in chloroform; cell length = 10 cm).

In the tests described below, the following compounds are employed:



Example A

Pre-emergence test

Solvent: 5 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol  
ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

Seeds of the test plants are sown in normal soil and, after 24 hours, watered with the preparation of the active compound. It is expedient to keep constant the amount of water per unit area. The concentration of the active compound in the preparation is of no importance, only the amount of active compound applied per unit area being decisive. After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of the untreated control. The figures denote:

0% = no action (like untreated control)

100% = total destruction

In this test, the active compounds according to the invention, according to Examples 1 and 2, show better herbicidal activity than the corresponding racemic compounds (A) and (B).

Table A

## Pre-emergence-Test

Active compound	Amount of active compound (kg/ha)	Activity (in %)			
		Dicotyledoneae *	Monocotyledoneae **	Beets	Soya beans Maize
(A) (known)	1	95,6	69,3	100	40 10
(B) (known)	1	81,4	61,4	100	0 0
(1) (inventive compound)	0,45	88,6	42,1	99	10 0
(2) (inventive compound)	0,51	77,1	74,1	99	0 0

\*) = average activity against several dicotyledon weeds

\*\*) = average activity against several monocotyledon weeds



Example B

Post-emergence test

Solvent: 5 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol  
ether

5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate  
10 is diluted with water to the desired concentration.

Test plants which have a height of 5 - 15 cm are sprayed with the preparation of the active compound in such a way as to apply the particular amount of active compound desired per unit area. The concentration of the spray liquor is so chosen that the  
15 particular amounts of active compound desired are applied in 2,000 litres of water/ha. After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of  
20 the untreated control. The figures denote:

0% = no action (like untreated control)

100% = total destruction

In this test, the active compounds according to the invention, according to Examples 1 and 2,  
25 show better herbicidal activity than the corresponding racemic compounds (A) and (B).

T a b l e B

Post-emergence-Test

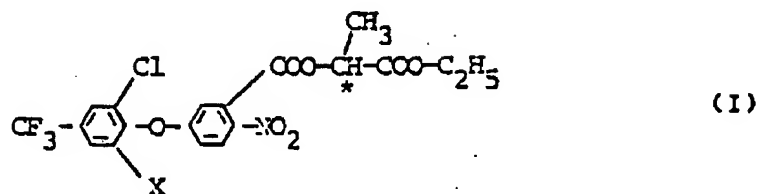
Active compound	Amount of active compound (kg/ha)	A c t i v i t y (in %)		Soya	
		Dicotyledoneae *	Monocotyledoneae **	Beets	beans Maize
(A) (known)	1	100	92	100	100 95
(B) (known)	1	99,9	89,1	100	99 95
(1) (inventive compound)	0,45	99,9	89,9	100	100 95
(2) (inventive compound)	0,51	99,9	83,3	100	99 100

\*) = average activity against several dicotyledon weeds

\*\*) = average activity against several monocotyledon weeds

Patent claims

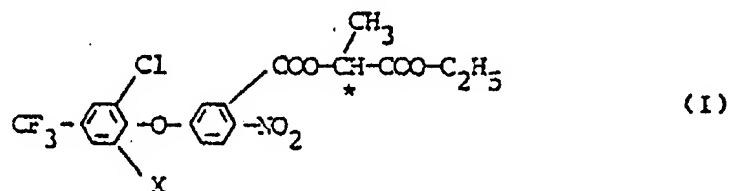
1. Dextrorotatory enantiomers of phenoxybenzoic acid derivatives of the formula



in which

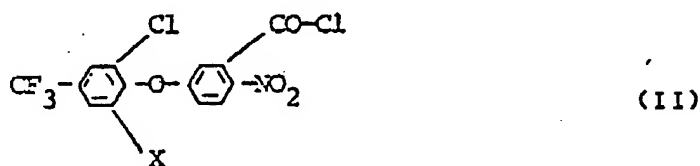
X represents hydrogen or chlorine.

2. Process for the preparation of the dextrorotatory enantiomers of the phenoxybenzoic acid derivatives of the formula



in which

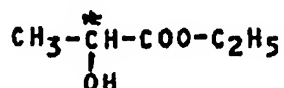
X represents hydrogen or chlorine, characterised in that phenoxybenzoic acid-chlorides of the formula



in which

X has the meaning given above, are reacted with the laevorotatory enantiomer of ethyl  
~~La A 21 598~~

lactate of the formula



(III)

if appropriate in the presence of an acid acceptor and if appropriate in the presence of a diluent.

3. A process as claimed in claim 2 and substantially as herein described or exemplified.
4. Dextrorotatory enantiomers of phenoxybenzoic acid derivatives whenever produced by a process according to either of claims 2 or 3.
5. Herbicidal agents, characterised in that they contain at least one dextrorotatory enantiomer of a phenoxybenzoic acid derivative as claimed in either of claims 1 or 4.
6. Use, as herbicides, of dextrorotatory enantiomers of phenoxybenzoic acid derivatives of the formula (I).
7. Process for combating weeds, characterised in that dextrorotatory enantiomers of phenoxybenzoic acid derivatives as claimed in either of claims 1 or 4 are applied to the weeds and/or their habitat.
8. Process for the preparation of herbicidal agents, characterised in that dextrorotatory enantiomers of phenoxybenzoic acid derivatives as claimed in either of claims 1 or 4 are mixed with extenders and/or surface-active substances.

18 MAR 1983



JOHN & KERNICK  
FOR THE APPLICANT.